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Note

Synthesis and molecular structure of the nitride $(L_{OEt})Mo(N)Cl_2$ $[L_{OEt} = (\eta\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3]$

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Abstract

Complex $(L_{OEt})Mo(N)Cl_2$ (**1**) ($L_{OEt} = (\eta\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$) was synthesized from the reaction of $MoCl_4(THF)_2$ with trimethylsilylazide, N_3SiMe_3, and, subsequently, with the sodium salt of the Kläui's ligand, NaL_{OEt}. Its structure was determined by single crystal X-ray diffraction. The apparently long molybdenum–nitride bond distance, 1.709(6) Å, was interpreted on the basis of the existence of random positional disorder within the crystal (*rotational disorder*). This fact was confirmed by the presence of an unusual short molybdenum–chloride length, 2.087(5) Å.

Keywords: Molybdenum; Nitride; Crystal structures; Disorder

1. Introduction

From the initial report of the first preparation of the monoanionic Kläui's type ligand [1], $L_{OEt} = [(\eta\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$, to our days a good number of transition metal complexes and main group derivatives containing this tripod ligand [2] or related [3] have been synthesized and characterized. The field has been extensively developed by Kläui et al. [4], although also some other groups have used this ligand as a stabilizing group in their chemistry [5]. Transition metal compounds simultaneously containing the Kläui's ligand and a multiple bonded ligand are known for the carbine [6], carbene [6a,7], vinylidene [7], allenylidene [8], imido [6a,9] and oxo [6a,10] functionalities. By the time in which our work started, no nitride species were known containing Kläui's coligand and we decided to prepare one example. While our work was in progress, nitride complexes of rhenium and osmium containing the Kläui's coligand have been structurally characterized [11].

The present paper is an extension of our work on high-valent molybdenum complexes [9,10] and here we report the synthesis and the structural characterization of a molybdenum(VI) complex containing the nitride ligand and the Kläui's coligand, namely $(L_{OEt})Mo(N)Cl_2$ (**1**). Apparently, elongated Mo–N and shortened Mo–Cl bonds in this complex can be understood in terms of random positional disorder in the unit cell. The term *rotational disorder* has been previously adopted for this phenomenon.

2. Experimental

2.1. Materials and methods

All preparations and other operations were carried out under dry oxygen-free nitrogen atmosphere following conventional Schlenk techniques. Solvents were dried and degassed before use. Microanalyses were carried out by the Microanalytical Service of the University of Sevilla. IR spectra were recorded on Perkin–Elmer Model 883 spectrophotometer. ^1H-, ^{13}C- and ^{31}P-NMR spectra were run on Bruker AMX-300 spectrometer. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C-NMR spectra were referenced

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using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. The petroleum ether used had b.p. 40–60 °C. The compound $MoCl_4(THF)_2$ [12] was prepared according to the literature procedure.

2.2. Preparation of $(L_{OEt})Mo(N)Cl_2$ (**1**)

To a suspension of freshly prepared $MoCl_4(THF)_2$ (0.154 g, 0.48 mmol) in Et_2O (40 ml) at −20 °C was added one equivalent of N_3SiMe_3 (0.5 M solution in THF). There was a slow evolution of dinitrogen. The mixture was gradually warmed at 30 °C and stirred at this temperature for 3 h. Over the resulting dark red solution was added NaL_{OEt} (0.26 g, 0.48 mmol) in Et_2O (15 ml) and the reaction mixture stirred overnight at room temperature. The solvent was removed in vacuo, the residue extracted with Et_2O, filtered and concentrated. Cooling the solution at −20 °C afforded the compound **1** as an orange–yellowish crystalline solid (60%). ^1H-NMR (Cl_3CD): δ 5.11 (s, 5, Cp), 4.20–4.09 (br s, 12, OCH_2), 1.28 (very br s, 18, CH_3). $^{31}P\{^1H\}$-NMR (Cl_3CD): AX_2 spin system, δ 114.3 (br d, $^2J_{PP} = 155$ Hz), 127.6 (br t). $^{13}C\{^1H\}$-NMR (Cl_3CD): δ 88.2 (Cp), 61.3 (d, $J_{CP} = 9.5$ Hz, CH_2), 60.9, 60.5 (t, $J_{CP} = 4.8$ Hz, CH_2), 15.1–15.0 (several br s, CH_3). Anal. Calc.: C, 28.4; H, 4.9; N, 1.9. Found: C, 28.5; H, 4.7; N, 1.0%. No satisfactory analytical data (N percentage) could be obtained for this compound.

2.3. X-ray crystallography

A summary of the fundamental crystal and refinement data are given in Table 1.

Table 1
Crystal data and structure refinement parameters for complex $(L_{OEt})Mo(N)Cl_2$

Compound	$(L_{OEt})Mo(N)Cl_2$
Empirical formula	$C_{17}H_{35}Cl_2CoMoNO_9P_3$
Formula weight	716.14
Temperature (K)	193(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	34.171(3)
b (Å)	10.6363(9)
c (Å)	17.674(2)
β (°)	118.078(1)
U (Å^3)	5667.6(8)
Z	8
D_{calc} (g cm^{-3})	1.679
μ (mm^{-1})	1.429
Θ Range (°)	2.58–23.29
Final R values [$I > 2\sigma(I)$]	$R = 0.0535$, $wR = 0.1373$

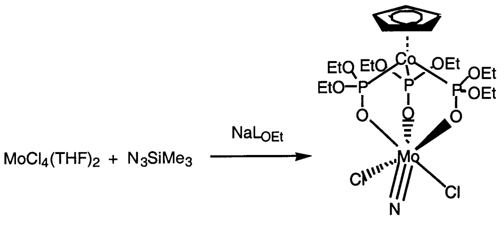
A crystal showing well defined faces was mounted on a Siemens Smart CCD detector diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo–K_α radiation) operating at 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of three sets exposures. Each exposure of 10 s covered 0.3° in ω. The crystal to detector distance was 6.05 cm. Coverage of the unique set was over 92% complete to at least 23° in θ. Unit cell dimensions were determined by a least-squares refinement using reflections with $I > 20\sigma(I)$ and $6 < 2\theta < 46°$. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lp effects. Full-matrix least-squares refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. H atoms were included in their calculated positions. Refinement on F^2 for all reflections, weighted R factors (wR) and all goodness-of-fit S are based on F^2, while conventional R factors (R) are based on F. Most of the calculations were carried out with SMART software for data collection and for data reduction and SHELXTL [13] for structure solution and refinement.

3. Results and discussion

3.1. Synthesis

The decomposition of azides is a classical synthetic route for the preparation of nitride transition-metal complexes [14]. In particular, the interaction of $MoCl_4(THF)_2$ or $MoCl_4(MeCN)_2$ compounds with trimethylsilylazide, N_3SiMe_3, provides an entry to nitride derivatives of molybdenum(VI) [15]. In situ reactions with trispyrazolylborate type ligands afford nitride complexes containing this monoanionic tridentate ligand [16]. Following the same synthetic strategy, the treatment of $MoCl_4(THF)_2$ with trimethylsilylazide, N_3SiMe_3, and, subsequently, with the sodium salt of the Kläui's ligand, NaL_{OEt}, yields complex $(L_{OEt})Mo(N)Cl_2$ (**1**) in medium yields (Scheme 1).

Complex **1** is soluble in Et_2O and other more polar solvents. It is monomeric and, contrary to the observed behaviour of '$Cp^*Mo(N)Cl_2$' [17], no tendency to aggregation was detected in solution. Moreover, **1** was recovered unaltered upon reaction with one equivalent



Scheme 1.

of in situ generated HCl, in contrast, for example, with the nucleophilic character exhibited by nitride ligand in $Mo(N)(S_2CNR_2)_3$ complexes [18] or in complex $Mo(N)(CH_2^tBu)_3$ [19].

3.2. Molecular structure of **1**

The crystal structure of $(L_{OEt})Mo(N)Cl_2$ (**1**) has been determined and the molecular geometry, together with the labelling scheme adopted, is shown in Fig. 1. Table 2 contains selected bond distances and angles. The complex has a distorted octahedral structure with the tripod L_{OEt} ligand leaving only one possible distribution for the nitride and chloride groups.

Some distinctive features appear in the bond distances of **1**. The Mo–N1 length, 1.709(6) Å, is long in comparison with the analogous distance found in the related $(Tp^*)Mo(N)(N_3)_2$ derivative, 1.646(4) Å [16b] or in other nitride-molybdenum(VI) complexes. Also, the Mo–N1 bond length is longer than the mean value of 1.649(4) Å obtained from the range 1.615–1.704 Å of Mo–nitride bond lengths [20]. In this range was not included complex $Mo(N_3)(N)(dppe)_2$ [21] for which the Mo–N distance of 1.79(2) Å is unusually long. Additionally, the Mo–Cl1 bond distance, 2.087(5) Å, is unusually short. A CSD search gave a mean value of 2.415(1) Å for the Mo–chloride bond distance (843 structures, range 2.02–2.90 Å). The Mo–oxygen bond distances are normal in comparison with other structurally characterized complexes of Mo and W that contain Kläui's type ligands (range 2.12–2.21 Å) [22]. The typical *trans* influence of the nitride ligand [23] was manifested in the Mo–O11 distance, 2.173(5) Å. However, a similar lengthy distance is also observed for the Mo–O31 bond, 2.131(7) Å, precisely that occupying the *trans* position with respect to the abnormally short Mo–Cl1 bond. This distance is longer than the third Mo–O21 length, 2.058(6) Å.

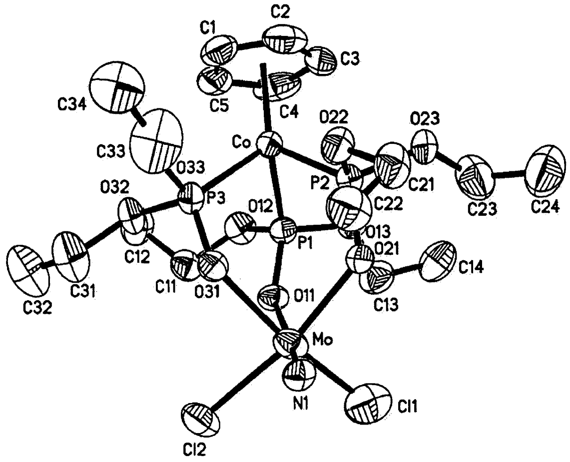


Fig. 1. Molecular structure of $(L_{OEt})Mo(N)Cl_2$ (**1**).

Table 2
Selected bond distances (Å) and angles (°) for complex **1**

Bond distances			
Mo–N1	1.709(6)	Mo–O11	2.173(5)
Mo–Cl 1	2.087(5)	Mo–O21	2.058(6)
Mo–Cl 2	2.346(3)	Mo–O31	2.131(7)
Bond angles			
O21–Mo–O31	83.6(3)	N1–Mo–O11	172.1(3)
O31–Mo–O11	81.1(2)	N1–Mo–Cl 2	97.4(3)
O21–Mo–O11	81.8(2)	Cl 1–Mo–O31	168.4(2)
O31–Mo–Cl 2	88.8(2)	O21–Mo–Cl 1	90.5(2)
O21–Mo–Cl 2	164.7(2)	Cl 1–Mo–O11	88.2(2)
O11–Mo–Cl 2	83.9(2)	Cl 1–Mo–Cl 2	94.6(2)
N1–Mo–O31	91.1(3)	N1–Mo–Cl 1	99.4(3)
N1–Mo–O21	96.0(3)		

After the reinvestigation of bond-stretch isomerism [24], Parkin has reviewed different types of crystallographic disorder [25]. As he stated, the most common source of crystallographic disorder comes from the existence of equivalent molecules in different orientations within the crystal. If the 'equivalent molecules' are diverse species (for example due to co-crystallization) the term *compositional disorder* was used [24,26]. If they are the same species the names *positional disorder* or *orientational disorder* were frequently adopted [24,27]. At the present, the random positional disorder of isoelectronic ligands is a well-known phenomenon [28].

All the structural data described above for **1** can be interpreted on the basis of *rotational disorder* in the crystal. This term has been recently employed by Mayer and co-workers [29] in the description of the disorder found in a related nitride-osmium $TpOs(N)Cl_2$ complex. This is a positional disorder, but the term *rotational* recalls the origin of that disorder. For example for **1**, there are two positions for the molecule in the crystal. Both are placed with the Mo–Co axe parallel, but in one of these positions the entire molecule is rotated 120° with respect to this axe. In such way, the nitrido ligand occupies the position of a chloride ligand (Cl1) and one chloride ligand that of the nitrido one. As a result of such disposition the global X-ray results are those commented, that is an apparent short Mo–Cl1 bond and an apparent long Mo–N1 bond.

4. Supplementary material

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Centre, CCDC No. 194413 for compound **1**.

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